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NATURAL ATTENUATION STUDY
FOR THE SANTA SUSANA FIELD LABORATORY

FINAL REPORT

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Santa Susana Field Laboratory Soil Treatability Studies
Task VI. Natural Attenuation Study

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Environmental Remediation Services for Environmental Compliance
for Area IV

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The final report for the first phase of the natural attenuation study was completed in May 2014. This report includes a summary of the conclusions of that report and a summary of additional natural attenuation conclusions based on additional information obtained from concurrent laboratory and field studies for Area IV of the Santa Susana Field Laboratory (SSFL); Area IV is referred to as "the site" in this document. These concurrent studies included a bioremediation study which examined bacteria and fungi found at the site and a microcosm study with soil collected from the site. Another study investigated the potential for plants to reduce contaminant concentrations through the process of phytoremediation. These studies provided valuable information that informs conclusions about natural attenuation specific to the site.

This natural attenuation study is one of five soil treatability studies commissioned by the US Department of Energy (DOE) to support the evaluation of methods for reducing the volume of contaminated soils that may need to be removed from Area IV of the (SSFL) by excavation, hauling, and disposal methods. The contaminants of interest (COIs) at the site include petroleum hydrocarbons (measured as extractable fuel hydrocarbons, EFH), polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated dioxins/furans, and heavy metals such as mercury and silver. Natural attenuation is defined as the reduction of contaminants at a site through natural processes. This reduction may occur through either biological processes such as biodegradation, and/or abiotic processes such as volatilization and photo-oxidation. The use of natural attenuation for remediation usually requires verification of the contaminant reductions and the mechanisms of these processes and field monitoring over time. The purpose of this study is to determine the natural processes operating at Area IV that are reducing or could reduce contaminant soil concentrations. In addition, the study was conducted to estimate the rates of natural attenuation at the site under current conditions.

The first phase of this study was a literature review to determine which soil COIs in Area IV are amenable to biodegradation and other natural attenuation processes, what biodegradation and natural attenuation pathways are known for the COIs, and what rates of natural attenuation of the contaminants have been observed in published field and laboratory studies. Estimates were made of the times required to reduce soil contaminant concentrations to acceptable levels using natural attenuation alone based on what was known of the site conditions at Area IV. The second phase of this study makes use of the findings of companion studies on bioremediation and phytoremediation of Area IV soils to make better site-specific predictions of natural attenuation rates. These companion studies include microcosm experiments to measure biodegradation rates of the contaminants in Area IV soils under natural attenuation conditions. The bioremediation study also includes an investigation of the microbial communities present in Area IV soils, and the results of that investigation are used here to provide an indication of what bacteria and/or fungi are present in the soils and which are known degraders of the contaminants.

The literature review of Phase I suggested that all of the COIs in Area IV soils are in theory amenable to natural attenuation processes such as volatilization, leaching, and phytoremediation (by existing vegetation at the site). Non-metal COIs are also amenable to biodegradation by bacteria and fungi. However, the rates of natural attenuation may be slow for COIs at the site because of the long time these COIs have been aging in the soil. Many of the COIs at the site have been in the soil for several decades, and during this time weathering processes such as volatilization, biodegradation and sequestration in the soil would be expected to have changed the composition and disposition of the COIs. For example, most of the lighter compounds may have volatilized during this weathering time, leaving behind contaminants with low volatility, which are by nature less likely to volatilize in the future. Similarly, the most biodegradable compounds are likely to have already biodegraded, leaving behind the more recalcitrant compounds (either original compounds or degradation products) at the site

Bacterial and fungal biodegradation appear to be the most likely processes to contribute to further reductions in concentrations of the non-metal COIs. Biodegradation processes were researched for each of the COIs, and the microorganisms capable of mediating biodegradation were listed for each COI. In addition, tables of published biodegradation rates under natural attenuation conditions are provided in the Phase I natural attenuation report for each COI. The potential for these processes to contribute to natural attenuation of each COI are described below, along with additional insights gained from the bioremediation and phytoremediation companion studies.

Petroleum hydrocarbons: Biodegradation of non-aromatic petroleum hydrocarbons in soils is well documented, and hydrocarbon-degrading microorganisms are nearly ubiquitous in the environment. However, some hydrocarbon compounds are more difficult to biodegrade than others, such as longer-chain hydrocarbons. Reported half-lives for biodegradation of the various petroleum hydrocarbons in soil range from days to several years. Based solely on published biodegradation rates, the time to reduce site petroleum hydrocarbon concentrations to the DTSC-specified background concentration for clean-up of 5.7 ppm would be 0.42 years for the more easily degradable petroleum hydrocarbons present at lower concentrations to 69 years for the more recalcitrant ones present at higher concentrations. This wide range is also due to the range of published rates of biodegradation of petroleum hydrocarbons. Since petroleum hydrocarbon contaminants at the site are highly weathered, the most rapid rates are not expected for ongoing natural attenuation at the site.

The field investigation conducted as part of the bioremediation study found many species of bacteria and fungi in site soil which have been reported in the literature to biodegrade hydrocarbons. Results of the unamended bioremediation microcosms indicated little or no

biodegradation of extractable fuel hydrocarbons (EFH) for any of the three soil samples Biostimulation with nitrogen and phosphorus fertilizer appears to have improved biodegradation significantly, with over 50% reduction in EFH concentration over 362 days. Addition of soy lecithin as a surfactant and rice hulls as a bulking material did not significantly improve observed biodegradation rates. Similarly, bioaugmentation with the white-rot fungi *Phanerochaete chrysosporium* had little or no effect on biodegradation rate. These results suggest that future biodegradation of petroleum hydrocarbons at the site will be limited under natural attenuation conditions. However, biostimulation with fertilizer is promising and should be further explored with field tests.

An important consideration for petroleum hydrocarbons is that the method of analysis used to quantify EFH may be erroneously including compounds considered to be natural organic material (NOM). Gas chromatography/mas spectroscopic (GC/MS) analysis of soil from Area IV indicates the presence of significant quantities of organic acids, such as palmitic acid. These compounds elute at the same time in the chromatograms as petroleum hydrocarbons, and thus when the peaks are integrated to determine EFH they erroneously elevate the measured EFH concentration. Experiments are currently underway in the Cal Poly lab to determine to what extent NOM may be contributing to measured EFH concentrations and to evaluate methods for removing NOM from the soil samples, such as a silica gel fractionation.

Polyaromatic hydrocarbons (PAHs): Numerous species of aerobic PAH-degrading bacteria and fungi have been reported in the literature. Their ability to biodegrade PAHs is dependent on the number of aromatic rings, with the slowest rates for PAHs reported for PAHs with the greatest number of aromatic rings, such as benzo-a-pyrene. Half-lives of 60 days to 3 years have been reported for biodegradation of PAH mixtures in soil. The time estimated to reach DTSC-specified background concentrations for clean-up for PAHs at the site (2.5 - 5.6 parts per billion, ppb) range from 5 to 15 years based on comparison to relevant published field studies. However, PAHs at the site have been highly weathered through 20-50 years of natural processes, such as degradation and sequestration, and these processes may have reduced their bioavailability. This decrease in bioavailability and the biodegradation of easily-degraded PAHs could increase their expected half-lives for ongoing natural attenuation at the site. The literature suggests that biodegradation rates may be accelerated by amending soils with surfactants to increase the bioavailability of the sequestered PAHs. Phytoremediation has been reported in some studies to be successful for PAHs, and data from one study suggests that the PAHs found in Area IV soils could be remediated to clean-up levels in 1.5 to 2.7 years with active phytoremediation.

Quantitative polymerase chain reaction (qPCR) analysis of DNA collected from Area IV soils did not detect aerobic or anaerobic genes associated with PAH biodegradation. Further, the

microcosm experiment did not show significant PAH biodegradation over a period of 244 days. Analysis of site data also indicated little to no PAH biodegradation over the recent five-year time frame. Despite some positive reports of phytoremediation of PAHs in the literature, the greenhouse experiments also found no significant changes in PAH concentrations in the soil of planted microcosms over the 211-day experiment.

Polychlorinated biphenyls (PCBs): PCB biodegradation is more complex than petroleum hydrocarbon biodegradation, often requiring a combination of anaerobic and aerobic conditions. Bacterially mediated PCB degradation typically involves anaerobic dechlorination followed by aerobic biodegradation. Only a few species of bacteria have been identified with the ability to reductively dechlorinate PCBs (the anaerobic step), and these are found mostly in aquatic sediments. Reported rates of PCB biodegradation are extremely low, even under ideal conditions. In fact, a half-life of 40 years was reported for Aroclor 1260, which is the predominant type of PCB found at the site. Since anaerobic conditions were not observed in site soils, bacterial dechlorination is unlikely. However, fungal biodegradation of PCBs may be possible at the site, because fungi do not require anaerobic conditions. Phytomediation of PCBs is also a possibility at the site, although limited uptake of PCBs by plants has been reported in the literature.

In the soil microcosm experiments, slight decreases were observed in concentrations of PCBs over the 8 month incubation period relative to sterile controls, but these decreases were not statistically significant at the 95% confidence level. In the phytoremediation study, soil PCB concentrations decreased by 13-15% over 7 months (relative to controls) for soil microcosms planted with purple needlegrass and coyote brush. Since no PCBs were observed in the plant tissue, and DNA analyses suggest that the plants may have changed the soil microbial community, the mechanism for this reduction appears to be stimulation of the bacteria or fungi in the root-zone of the plants in a process known as rhizostimulation. However, PCB adsorption to glass has been reported in the literature, and such adsorption may have contributed to PCB losses observed in the planted microcosms. These results suggest the possibility of further evaluation for using phytoremediation for PCBs.

Chlorinated Dioxins/Furans: Like PCBs, bacterial biodegradation of chlorinated dioxins requires a combination of anaerobic and aerobic processes. Since anaerobic conditions were not found in the site soils, this mechanism of biodegradation is unlikely. However, the literature suggests that fungi such as *Phanerochaete chrysosporium* are capable of mediating biodegradation of chlorinated dioxins under aerobic conditions. Limited research has been done on phytoremediation of dioxins, but some researchers suggest that its effectiveness for dioxins might be similar to that for PCBs. Based on the published literature, biodegradation of the

dioxins in site soils to clean-up levels could take 1 to 50 years under natural attenuation conditions.

Soil vapor analyses performed at the site as part of the bioremediation study confirmed that soils in Area IV are aerobic, suggesting that bacterially-mediated reductive dechlorination is not likely. Only small decreases in dioxin concentrations were observed in the unamended soil microcosms over 244 days of incubation, suggesting that dioxin biodegradation under natural attenuation conditions is very slow, and the longer end of the predicted range of remediation times would be expected in the field. Microcosms bioaugmented with the fungi *Phanerochaete chrysosporium* showed a slight improvement in dioxin biodegradation rate, but the effect of this treatment was not significant at the 95% confidence level.

Field testing of native plants as part of the phytoremediation study revealed chlorinated dioxins in the roots and foliage of some plant species growing in contaminated Area IV soils. Purple needlegrass picked up the highest concentrations of dioxins in the field tests, but the soil concentrations of dioxins were unaffected by planting with purple needlegrass in the greenhouse microcosm experiments. Coyote brush also picked up dioxins in the field tests and also resulted in decreases in soil concentrations of dioxins in the phytoremediation microcosms planted with coyote brush. These results suggest the possibility of further evaluation for using phytoremediation for chlorinated dioxins.

Perchlorate: Leaching into the underlying groundwater is likely to be an important mechanism of natural attenuation of soil perchlorate contamination because of its high solubility in water. Biodegradation of perchlorate requires anaerobic conditions, which are not likely to be present for Area IV soils. Fungal biodegradation of perchlorate has not been reported. Phytoremediation may enhance perchlorate remediation in site soils based on one published study, but this study was done with saturated soil, and thus may not be applicable to SSFL. Perchlorate degradation was not investigated in the SSFL bioremediation or phytoremediation companion studies.

Mercury: The literature review suggests that volatilization of elemental mercury and/or methyl mercury is a possible natural attenuation mechanism for mercury removal from site soils, but that this process is likely to be very slow, and it could create air pollution issues. Phytoremediation of mercury is a potential method of removing mercury from the soil, although this would not be a natural attenuation method since it would involve active removal of plants from the site. It is unlikely that plants at the site will take up mercury into their roots unless the mercury is first chelated. However, mercury uptake by plants was not observed in either field assays at the site or greenhouse experiments even with the addition of the chelating agent EDTA.

Silver: Since silver is a metal, like mercury, it will not biodegrade. Some uptake of silver was observed in roots and foliage of one or two species of plants tested in the field and in greenhouse experiments, but the amount of silver accumulated would not warrant use of phytoremediation for silver removal from the soil.

General conclusions:

Estimates of times predicted to reach proposed clean-up levels via natural attenuation based on the Phase I literature review varied widely, from under 1 year to over 50 years, depending on the COI and their varying concentrations across the site. Since the Phase I literature review, site-specific information has been obtained (Phase II), both in terms of redox conditions in the soil and results from extensive site-specific research on biodegradation and phytoremediation in two companion studies. As described above for each COI, these Phase II site-specific studies suggest that the estimated times for remediation would be expected to be at the long ends of the Phase I estimates. Thus, natural attenuation at SSFL is expected to take on the order of decades to reach DTSC-specified background concentration for clean-up.

The slow biodegradation rates observed in the bioremediation and phytoremediation studies are likely the result of extensive weathering of the contaminants at the SSFL site through the past 20-50 years of on-going natural attenuation processes. It is highly unlikely that natural attenuation rates would accelerate at the site without active remediation. Natural attenuation processes often follow first-order kinetics, which means that the rates of natural attenuation would decrease over time as the contaminant concentrations decrease. In addition, biodegradation typically slows down even more than expected from first-order kinetics over time as contaminants become sequestered in the soil. Also, the most easily biodegraded components of the contaminants typically biodegrade early in the natural attenuation process, leaving the more recalcitrant compounds (either original compounds or degradation products) at the site.

The bioremediation and phytoremediation studies suggest some promise for more active remediation strategies. The most promising of these strategies is biostimulation of petroleum hydrocarbon biodegradation by fertilizer addition. Phytoremediation could potentially accelerate natural attenuation of chlorinated dioxins and/or PCBs, but likely to a limited extent.

In some cases, long remediation times are predicted because the current DTSC-specified clean-up levels for the site requires reaching very low background levels. Much shorter remediation times would be expected if clean-up levels were set similar to those set for typical industrial sites. Natural attenuation should be considered on a case-by-case basis for the different sub-areas in Area IV. Soils with very high contaminant concentrations will likely need to be excavated and hauled off site, but natural attenuation should be considered for soils with lower

contaminant concentrations where the length of time required for reaching cleanup levels would not be an issue. This could greatly reduce the quantity of soil that needs to be excavated and the many associated environmental impacts of such excavation. Although the focus of this investigation was on natural attenuation, the findings suggest that more active bioremediation methods should also be further explored.